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Removing Fermi Resonance through Deuterated Molecules with Single C–H Bond in C-H Stretching Region of Raman Spectra[†]

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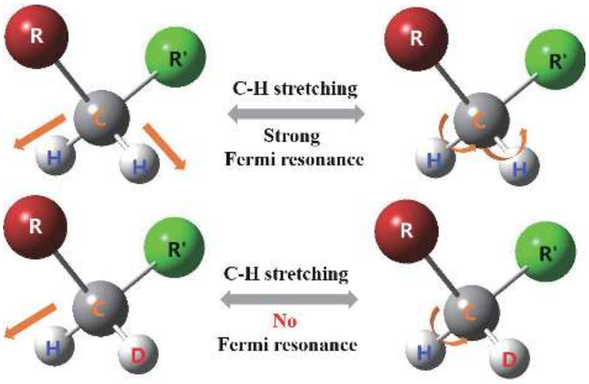
The Raman spectra in the C-H stretching region are of great importance for the study of the structure and dynamics of organic compounds. However, the Fermi resonance between the first overtone mode of C-H bending vibration and C-H stretching vibration typically results in the disturbance of Raman bands in the C-H stretching region. In this context, a specific deuterated molecule with only one C–H bond was proposed, and it was found that the frequency of the first overtone mode of the C-H bending vibration was significantly different from the frequency of the C-H stretching vibration. Due to the significant discrepancy, Fermi resonance in the C-H stretching region was eliminated from the experimental and theoretical Raman spectra of deuterated leucine, deuterated benzoin, deuterated methanol, and deuterated ethanol. Hence then, the Raman spectra of these specific deuterated compounds in the C-H stretching region can be used to study the structure or the dynamics of the organic compounds.



Key words: Fermi resonance, C-H stretching vibration, Raman spectra, C-H bending vibration, Overtone

I. INTRODUCTION

The significance of bio-molecules to living organisms cannot be overstated. Vibrational spectroscopy in the C-H stretching region represents a significant technological advancement in the exploration of bio-molecules, with applications spanning a multitude of domains. To illustrate, stimulated Raman scattering (SRS) microscopy in the C-H stretching region was employed to visualize saturated and unsaturated fatty acids, thereby offering a novel approach to label-free imaging [1, 2]. Similarly, SRS microscopy in the C-H stretching region was also deployed to detect the neuronal membrane potential [3]. These findings directly demonstrate the utility of vibrational bands in the C-H stretching region.

The basis of these applications is the assignment of vibrational bands in the C-H stretching region. However, the strong spectral overlap and the Fermi resonance (FR) pose significant challenges to the accurate assignment of vibrational bands in this region. The phenomenon of Fermi resonance (FR), first observed by Fermi in the vibrational spectrum of CO_2 in 1929, refers to the resonance between the fundamental band and the overtone band. As a result, the resonance can amplify the spectral intensity of the overtone band, making it difficult to identify spectral peaks. As an illustrative ex-

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ample, the IR and Raman spectra of methanol should show a single symmetrical stretching band within the C-H stretching region. However, the IR and Raman spectra showed the presence of three symmetrical bands. These bands were attributed to the FR between the CH_3 symmetric stretching vibration and the CH_3 bending overtone vibration. Accordingly, the band observed at about 2845 cm^{-1} is attributed to the CH_3 symmetric stretching vibration, while the bands observed at about 2925 cm^{-1} and 2955 cm^{-1} are attributed to the overtone of the CH_3 bending vibration [4]. Apart from the CH_3 group, FR also occurs in the spectrum of the CH_2 stretching vibration region [5]. Given the widespread occurrence of CH_3 and CH_2 groups in organic compounds, it is plausible that FR may be present in the vibrational spectrum of the C-H stretching region. In addition, FR not only complicates the assignment of the spectrum, but also directly interferes with the study of the microstructure of the molecular system. For example, in the C-H stretching region, FR can hinder the identification of the ethanol conformer and the study of the orientation of methanol at the interface. It is therefore essential to either control or eliminate FR.

Previous research has shown that there are two main methods of controlling FR. Firstly, the regulation of molecular interactions has been shown to influence FR. For example, changes in temperature [6] and solution pressure [7, 8], as well as the use of different solvents [9], can influence the phenomenon of FR. Secondly, the vibrational energy level can be altered by isotope substitution, which in turn affects FR. For example, previous studies [10] have shown that $^{13}CO_2$ has a reduced FR intensity compared to $^{12}CO_2$. Furthermore, when the molecule PyrNNN is labelled as $PyrN^{15}N^{15}N$, FR is inhibited [11].

A previous study of deuterated isopropanol [12] showed that the FR is absent in the C-H stretching region of the methanetriyl group (>CH-), implying that the FR may disappear in the spectrum of a single C-H stretching vibration. In this study, we carried out a comprehensive analysis of the Raman spectra of a number of organic compounds, each containing a single C–H chemical bond or a single C–D chemical bond. The molecules L-leucine-2-d1, (DL)-benzoin, (DL)-benzoin-d10 and tartronic acid contain the methanetriyl group (>CH-). The other molecules, deuterated alcohols, contain a single C–H chemical bond of methyl group (CD_2H-) or methanediyl group (-CDH-). It was observed that the FR was absent in all spectra within the single C–H bond or C–D bond stretching region. Theoretical calculations based on the B3LYP/6-311+G(d,p) method showed that the reason for the disappearance of the FR is that the frequency of the C-H bending overtone is significantly different from that of the C-H stretching vibration. Consequently, the spectra in the C-H stretching region without FR can be used to study the local structure of the molecules.

II. MATERIALS AND METHODS

A. Materials

Tartronic acid (98%) was purchased from Aladdin. (DL)-benzoin (99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (DL)-benzoin-d10 (99.2%), L-leucine-2-d1 (98.8%) and methanol-d2 (98%) were purchased from CDN Isotopes. These samples were used without any purification.

B. Experiments

The Raman spectrometer used in this study was constructed in-house. A comprehensive description of the Raman spectrometer can be found in our previous publication [13, 14]. The spectrometer consisted of a three-stage monochromator (Omni λ-180D & Omni λ-5008i) from Beijing Zhuoli Hanguang Instrument Co., Ltd. and an electrically cooled CCD (DR-316B-LDC-DD) from Andor and a continuous wave laser (GenesisMX532-1000, 532 nm) from Coherent. The laser beam was directly polarized using a Glan Laser prism, and the direction of polarization was subsequently controlled using a half-wave plate. The laser power was approximately 500 mW and the laser beam was focused onto the sample using an objective lens. The Raman spectra were recorded using the same objective and a backscatter configuration. The spectral resolution is approximately 2.0 cm^{-1} and the Raman shift of all spectra was calibrated against standard Raman spectra of ethanol.

C. Theoretical calculations

For theoretical calculations, the Gausssian-09 software package was used. In recent years, density functional theory with B3LYP and the basis set 6-311+G(d,p) was successfully used to optimize the stable conformers of some organic molecules and calculate the vibrational spectra of the corresponding molecules

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[15]. In this work, the same calculation method and basis set was also employed to optimize the structure of benzoin, tartronic acid, leucine, serine, methanol, ethanol, and propanol. The vibrational spectra of these molecules and the deuterated molecules were also calculated with the same method. To compare with the experimental spectra, the theoretical Raman spectra were plotted with a scaled factor of 0.97.

III. RESULTS AND DISCUSSION

A. Raman spectra of L-leucine-2-d1, benzoin, benzoin-d10, and tartronic acid

The IR spectra, Raman spectra, sum of frequency generation spectra of organic compounds in the C-H stretching region are significant in various fields, however FR in this region usually disrupts the application of the vibrational spectra. For example, FR presents in the C-H stretching region of methyl group [4, 5, 16] and methanediyl group [5, 16]. However, in recent C-H stretching region of methanetriyl group in iso-propanol [12] and mandelic acid [17], the FR was absent in the Raman spectra of C-H stretching region. Hence then, we systematically check whether the FR indeed is absent in the Raman spectra of the molecules with methanetriyl group in the C-H or C-D stretching region.

In this study, we selected a number of key molecules that include the methanetriyl group, namely L-leucine-2-d1, benzoin, benzoin-d10, and tartronic acid. Leucine is an amino acid that has been demonstrated to be effective in the prevention of muscle loss due to its ability to break down and convert to glucose at a faster rate. Benzoin is a raw material for organic synthesis, employed in the manufacture of bibenzoyl and phenytoin. Tartronic acid is a widely utilized medicinal agent, capable of inhibiting the conversion of sugars into fat within the human body, preventing the accumulation of body fat and exerting a weight-loss effect and coronary heart disease prevention effect. The chemical formulas of these molecules are all provided in FIG. 1.

The leucine molecule contains a methanetriyl group, a methanediyl group and a methyl group. The C-H stretching vibration bands of these groups overlap, making observation of the C-H stretching vibration band of the methanetriyl group of leucine challenging. In order to record the Raman spectra of the methanetriyl group, the COO-CH-NH_3^+ group was altered to COO-CD-NH_3^+ (see inset figure in FIG. 1(a)). Therefore, the vibration of the deuterated methanetriyl group would be distinct from that of the methanetriyl group. In the C-D stretching vibration, a single vibrational band was observed at ~2240 cm^{-1}, as illustrated in FIG. 1(a). This vibrational band was in accordance with the band in the theoretical Raman spectra of the deuterated leucine. Consequently, both the experimental and theoretical spectra demonstrated that FR was absent in the C-D stretching region of the deuterated methanetriyl group.

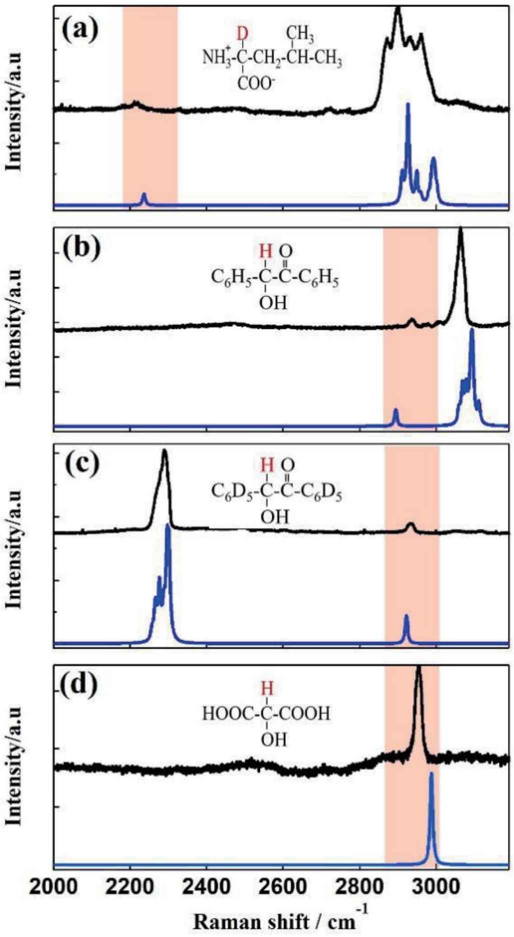

FIG. 1 Experimental (black) and theoretical (blue) Raman spectra of L-leucine-2-d1 (a), benzoin (b), benzoin-d10 (c), and tartronic acid (d).

The benzoin molecule is comprised of a methanetriyl group and a phenyl group. The C-H stretching vibrations of these two groups exhibit significant differences. Typically, the frequency of the C-H vibration of the phenyl group is greater than 3000 cm^{-1}, while the frequency of the C-H stretching vibration of the methanetriyl group is less than 3000 cm^{-1}. As illustrated in FIG. 1(b), within the spectral region below 3000 cm^{-1}, the experimental Raman spectrum of ben-

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zoin exhibits a single vibrational band. It can be reasonably deduced that the band observed below 3000 cm^{-1} is attributed to the C-H stretching vibration of the methanetriyl group of benzoin, while the band observed above 3000 cm^{-1} is attributed to the C-H stretching vibration of the phenyl group of benzoin. The experimental Raman spectrum is in accordance with the theoretical Raman spectra of benzoin. To eliminate the potential for disruption to the C-H stretching vibration of the phenyl group, Raman spectra were also recorded for the deuterated benzoin, in which the C–H bond of the phenyl group was replaced with a C–D bond. The chemical formula of the deuterated benzoin is provided in the insert of FIG. 1(c). Therefore, the C-D stretching vibrational band is located at approximately 2310 cm^{-1}, and there is only one single band in the C-H stretching region. The experimental Raman spectrum of the deuterated benzoin was also in agreement with the theoretical Raman spectra. Consequently, it can be concluded that FR was absent in the C-H stretching region of the methanetriyl group of benzoin.

In contrast to the leucine and benzoin molecule, the tartronic acid molecule contains only one C–H bond as part of the methanetriyl group. The Raman spectrum of tartronic acid was recorded and is presented in FIG. 1(d). In the region of C-H stretching, a single band is observed. Additionally, the theoretical Raman spectrum of tartronic acid exhibits a single band. There is a slight discrepancy between the experimental and theoretical frequencies of the C-H stretching vibration of the methanetriyl group, which may be attributed to the interaction of the solid tartronic acid. The presence of a single vibrational band in the spectra indicates that FR is absent in the C-H stretching region of the methanetriyl group of tartronic acid.

In these Raman spectra of the C-H and C-D stretching vibrations of the methanetriyl group, the FR is absent in this spectral region. The methanetriyl group is present in numerous organic compounds, including amino acids and certain pharmaceuticals. Consequently, the C-H stretching band of the methanetriyl group in these molecules can be employed to investigate the local structure and intermolecular interactions of the molecules in complex environments.

B. Raman spectra of deuterated methanol

Although the C-H or C-D stretching region of the methanetriyl group lacks the presence of FR, the methyl and methanediyl groups are more prevalent in organic compounds. In a previous study of the Raman and IR spectra of organic compounds with methyl and methanediyl groups, the presence of FR was typically observed in the C-H stretching region. In the aforementioned Raman spectra of organic compounds with a methanetriyl group, there is no evidence of FR in the C-H stretching region, which implies that there is no FR in the individual C–H bond vibrational spectrum. Therefore, deuterium atoms can be employed to substitute for some hydrogen atoms in the methyl and methanediyl groups. For instance, the $-CH_3$ group can be transformed into a $-CD_2H$ group, and a $-CH_2-$ group can be altered to a -CDH- group. This results in a single C–H bond remaining in the methyl and methanediyl group. The objective of this study is to ascertain whether the aforementioned FR can be eliminated from the Raman spectroscopy of these specific deuterated species within the C-H stretching region.

To illustrate this issue, the Raman spectrum of methanol was considered. Here, the FR is observed in the C-H stretching region. A previous study demonstrated that the strong bands at ~2925 cm^{-1} and ~2955 cm^{-1} were assigned to two FR modes of CH_3 bending overtones in the Raman spectrum of gaseous methanol [4]. Furthermore, in the IR spectra of CD_2H-OH multilayer and the corresponding methoxy adlayer on Ni(100) surface, FR between the C-H stretching fundamental vibration and the C-H bending overtone vibration was absent [18]. Here, we also record the Raman spectrum of deuterated methanol (CD_2H-OH) to study why the FR is absent in the C-H stretching region.

The Raman spectra in the C-H bending and C-H stretching region for liquid CH_3-OH and liquid CD_2H-OH were recorded, and are plotted in FIG. 2. In the Raman C-H bending region of CH_3-OH, the strongest band is located at ~1450 cm^{-1}. Consequently, the overtone modes of the C-H bending vibration are expected to occur around 2900 cm^{-1}. This frequency is in close proximity to that of the CH_3 symmetrical stretching vibration, which leads to the conclusion that the FR is evident in the C-H stretching region. The band observed at 2830 cm^{-1} is attributed to the CH_3 symmetrical stretching vibration, while the two bands observed at ~2910 cm^{-1} and ~2937 cm^{-1} are assigned to the FR vibrational modes of the methyl group. However, the Raman spectra of CD_2H-OH exhibit a markedly different

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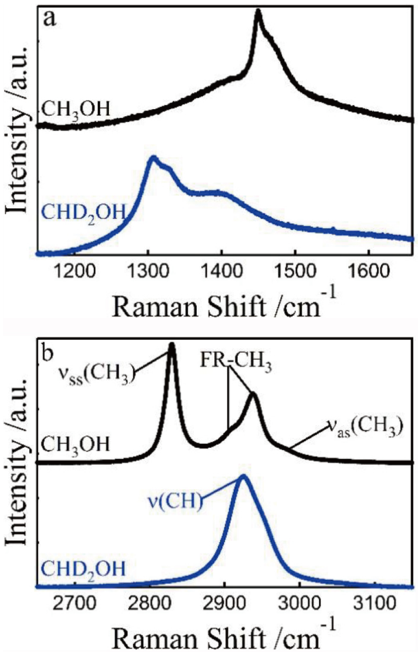

FIG. 2 The experimental Raman spectra of methanol (CH_3-OH) and deuterated methanol (CD_2H-OH) in the C-H bending vibration region (a) and in the C-H stretching vibration region (b).

profile compared to those of CH_3-OH. To illustrate, in the C-H bending vibration, the strongest C-H vibrational band is situated at ~1308 cm^{-1}. Consequently, the potential overtone of this mode is located near ~2619 cm^{-1}. The frequency differs considerably from that of the C-H stretching vibration. Consequently, in the typical C-H stretching region, the FR is absent. Furthermore, in the C-H stretching region, a single dominant band is observed. This band is therefore assigned as the stretching vibration of the single C–H bond of CD_2H-OH. The shape of this band is slightly anti-symmetrical, which may be attributed to the presence of two distinct C–H bonds in the deuterated methyl group. Given that the methyl group is capable of rotation along the C–O bond, the single C–H bond would exhibit variation when the C–H is in and out of the C-O-H plane. The existence of these two types of C–H bonds was also investigated through the analysis of the polarized Raman spectrum of methanol [4].

In order to gain theoretical insight into the manner by which this deuterated strategy regulates FR in the C-H stretching Raman spectra, we calculated the theoretical Raman spectra of methanol and deuterated methanol using density functional theory. The theoretical Raman spectra of CH_3OH are presented in FIG. 3(a). Given that the methyl group contains three C–H bonds, there are three distinct C-H stretching vibrational modes and three C-H bending vibrational modes. The theoretical calculation demonstrated that the three C-H stretching vibrational modes were the CH_3 symmetrical stretching mode, the C-H out-of-plane stretching mode, and the C-H in-plane stretching mode, respectively. The three distinct C-H bending vibrational modes were designated as γ_1, γ_2, and γ_3, respectively. In order to simulate the frequency of the first C-H bending overtone vibration, the frequency of the C-H bending vibration is multiplied by two. The resulting spectrum of the first C-H bending overtone mode is also plotted in FIG. 3(a). It is evident that the spectrum of the first C-H bending overtone mode is overlapped with the spectrum of the C-H stretching mode, which is why the FR is strong in the experimental Raman spectra of methanol.

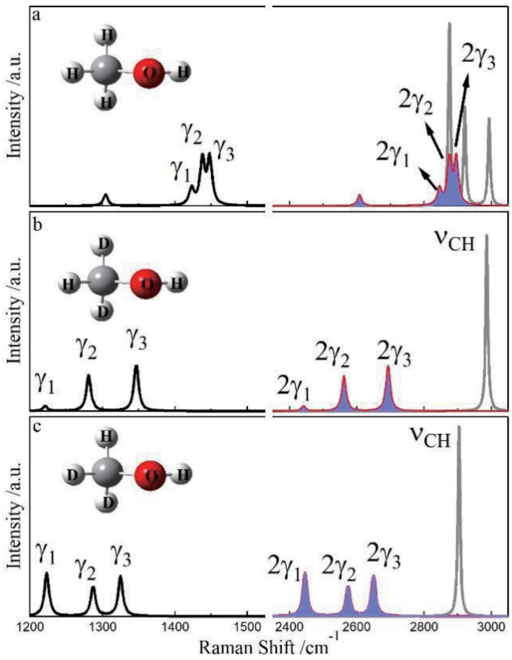

FIG. 3 (a) The theoretical Raman spectra of methanol (CH_3-OH); (b) and (c) deuterated methanol (CD_2H-OH) in the C-H bending vibration region and the C-H stretching vibration region, with H atom situated in either the C-O-H plane or out of the plane, respectively.

Furthermore, the Raman spectrum of deuterated methanol (CD_2H-OH) was also calculated using density functional theory. As with the methyl group of methanol, there are two types of C–H bond: one is in the plane of C-O-H, and the other is out of the plane of C-O-H. Consequently, two types of deuterated methanol were calculated. The Raman spectra of CD_2H-OH, with the H atom situated in either the C-O-H plane or out of the plane, are presented in FIG. 3 (b) and (c).

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In the C-H stretching region, only one Raman band was observed, while in the C-H bending region, three vibrational bands were observed. The frequencies of the bending modes of CD_2H-OH are considerably smaller than those of the bending modes of CH_3OH. Consequently, the frequencies of the first bending overtone modes are markedly different from the frequency of the C-H stretching mode. Therefore, FR is absent in the experimental Raman spectra of CD_2H-OH.

The aforementioned experimental and theoretical deuterated methanol studies have demonstrated that the replacement of two hydrogen atoms by two deuterium atoms in a methyl group can have a significant impact on the C-H bending vibration, resulting in a notable discrepancy in the frequency of the first overtone mode of the C-H bending vibration compared to that of the C-H stretching vibration. This pronounced disparity leads to the absence of the FR in the C-H stretching vibration region.

C. Raman spectra of deuterated ethanol

Similarly, ethanol is a type of alcohol, as is methanol. Ethanol is the predominant species present in the beverage and is frequently employed as a molecular model to investigate the interaction between water and amphiphiles. The spectra of ethanol in the C-H stretching region are of great importance for the study of structure and dynamics of ethanol. Indeed, the assignments of the bands in the Raman spectra of ethanol have been the subject of recent decades of research. In previous studies, the use of deuterated ethanol (CH_3-CD_2-OH and CD_3-CH_2-OH) enabled the distinction to be made between the contributions of the methyl group and the methanediyl group in the C-H stretching vibrational region [5]. It was found that the FR peaks were particularly strong in this region. As demonstrated in our previous Raman spectrum [19] of deuterated ethanol (CD_3-CH_2-OH and CD_3-CDH-OH), the FR peaks were clearly visible in the spectrum of solid ethanol, while they were absent in the liquid ethanol spectrum. Moreover, the absence of FR peaks in the C-H stretching vibration spectrum of CD_3-CDH-OH was also observed. The disappearance of the FR of the C-H stretching vibration of this deuterated methanediyl can be attributed to the significant difference in frequency between the C-H bending overtone mode and the C-H stretching vibration.

Prior to this study, the FR of the deuterated methyl group of ethanol had not been investigated. In this study, we employ density functional theory to calculate the Raman spectrum of deuterated ethanol (CD_2H-CD_2-OH). Ethanol exhibits two distinct conformations of the hydroxyl group along the C–O bond, designated as *trans*- and *gauche*- conformers, respectively. In the *trans*- configuration of ethanol, the dihedral angle of the HO–CC bond is approximately 180°, whereas in the *gauche*- configuration, it is approximately ±60°. In our previous Raman spectra of CD_3-CH_2-OH and CD_3-CDH-OH, the vibrational bands of these two conformers were observed [19]. In this study, the theoretical Raman spectrum of CD_2H-CD_2-OH was calculated to ascertain whether the FR was absent in the C-H stretching vibration of the deuterated methyl group (CD_2H-).

To facilitate a comparative analysis of the C-H stretching vibration of the CD_2H- group, the Raman spectrum of the -CH_3 group was also calculated for the CH_3-CD_2-OH molecule. The Raman spectra of the *trans*- and *gauche*- conformers of CH_3-CD_2-OH are presented in FIG. 4 (a) and (e), respectively. In the theoretical spectra, the smallest frequency difference between the first overtone modes of the CH_3 bending vibration and the CH_3 stretching vibration is ~28 cm^{-1} and ~27 cm^{-1} for *trans*- and *gauche*- CH_3-CD_2-OH, respectively. The frequency difference is sufficiently small to allow for the observation of FR in the C-H stretching vibration of CH_3-CD_2-OH.

The methyl group of ethanol comprises three distinct hydrogen atoms, resulting in the formation of three unique CD_2H-CD_2-OH molecules. These molecules are illustrated in FIG. 4. Given that the molecule contains a single C–H bond, the theoretical spectra exhibit a single C-H stretching band in the Raman spectra of these CD_2H-CD_2-OH molecules. In these Raman spectra, it was observed that the frequency of the first overtone mode of the CH bending vibration was markedly different from that of the C-H stretching vibration. To illustrate, the smallest frequency difference is approximately 371 cm^{-1} and 367 cm^{-1} in the *trans*- and *gauche*- CD_2H-CD_2-OH molecules, respectively. Therefore, the absence of the FR in the C-H stretching region can be attributed to the significant discrepancy between the frequencies of the first overtone mode of the C-H bending vibration and the C-H stretching vibration.

D. Raman spectra of deuterated propanol

In addition to methanol and ethanol, the FR was ob-

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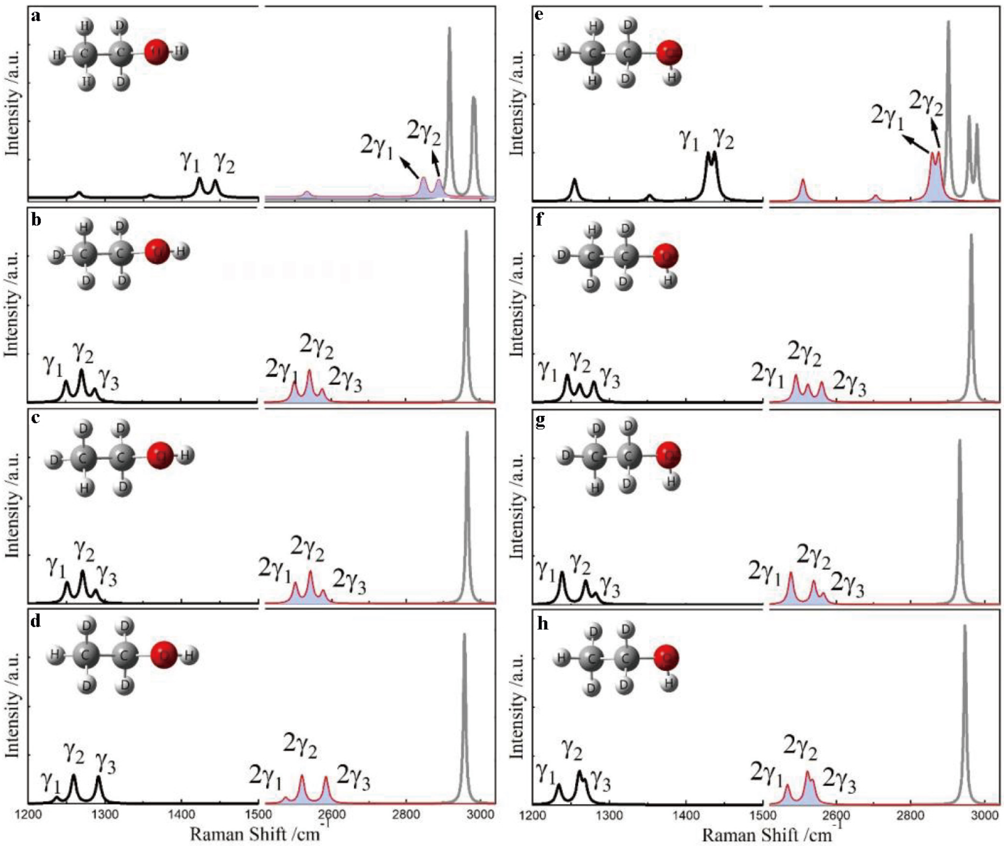

FIG. 4 The theoretical Raman spectra of *trans*- (left column) and *gauche*- (right column) ethanol in the C-H bending vibration region and the C-H stretching vibration region. (a, e) The spectra of CH_3CH_2OH, (b, f) the spectra of CD_2H-CD_2OH in which the H atom in the methyl group is above the C-C-O plane, (c, g) the spectra of CD_2H-CD_2OH in which the H atom in the methyl group is below the C-C-O plane, (d, h) the spectra of CD_2H-CD_2OH in which the H atom in the methyl group is in the C-C-O plane.

served in the C-H stretching vibration of iso-propanol [12] and normal propanol [16]. Conversely, the FR was absent in the C-H stretching vibration of the methyltriyl group of iso-propanol [12]. In this instance, the Raman spectra of the deuterated propanol were also calculated. To illustrate, the theoretical Raman spectra of CD_3-CD_2-CH_2-OH and CD_3-CD_2-CDH-OH were calculated and plotted in FIG. 5 for the deuterated α-methanediyl group (-CDH-).

Furthermore, the impact of deuterated propanol skeleton conformation on Raman spectra was investigated. In fact, *n*-propanol exists in five different conformations. The Raman spectra of these five conformations were all calculated. For the sake of clarity, only the spectra of the two distinct conformers, *trans*- and *gauche*- *n*-propanol, are presented here. In the *trans*-*n*-propanol, the dihedral angles of the CC–CO and CC–OH bonds are both approximately 180°. In this *gauche*-*n*-propanol, the dihedral angle of CC–CO is approximately −60°, while the dihedral angle of CC–OH is approximately 60°. The Raman spectra of the *trans*-*n*-propanol are presented in the left column of FIG. 5, while the Raman spectra of the *gauche*- *n*-propanol are presented in the right column of FIG. 5.

In the Raman spectra of CD_3-CD_2-CH_2-OH, the frequency of the overtone mode of C-H bending vibration was found to be similar to that of the C-H stretching vibration. This indicates that FR is evident in the C-H stretching region of CD_3-CD_2-CH_2-OH. Furthermore, the Raman spectra of CD_3-CD_2-CDH-OH revealed a significant discrepancy between the frequencies of the overtone mode of C-H bending vibration and the frequency of the C-H stretching vibration. To illustrate, in the case of *trans*- *n*-propanol, the smallest frequency difference between the C-H bending overtone mode and the C-H stretching mode is approximately 184 cm^{-1}. In *gauche*- *n*-propanol, the smallest frequency difference between the C-H bending overtone mode and the C-H stretching mode is 216 cm^{-1}. Therefore, it can be concluded that FR should be absent in the C-H stretching

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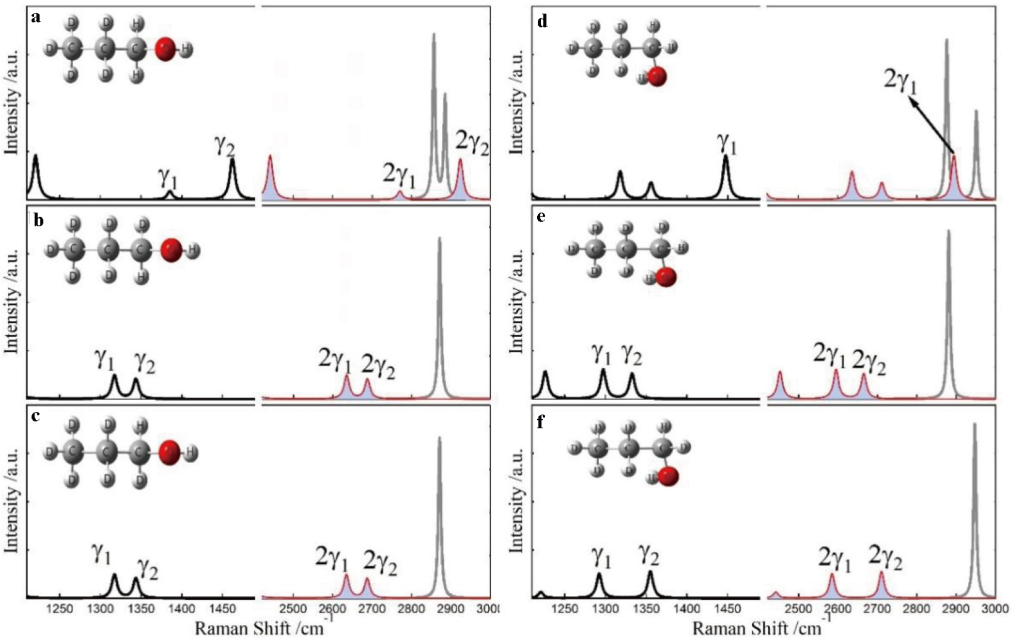

FIG. 5 The theoretical Raman spectra of *trans*- (left column) and *gauche*- (right column) propanol in the C-H bending vibration region and the C-H stretching vibration region. (a, d) The spectra of CD_3-CD_2-CH_2-OH, (b, c) the spectra of *trans*-CD_3-CD_2-CDH-OH in which the D atom in the α-methanediyl group is below and above the C-C-C plane, (e, f) the spectra of *gauche*- CD_3-CD_2-CDH-OH in which the D atom in the α-methanediyl group is in and above the C-C-C plane.

vibration region of CD_3-CD_2-CDH-OH.

In addition to the Raman spectra of the deuterated α-methanediyl group in propanol, the deuterated β-methanediyl group (-CDH-) and the deuterated methyl group (-CD_2H) of propanol were also calculated and included in Supplementary materials (SM). Furthermore, it was determined that the frequency of the C-H bending overtone mode was significantly disparate from that of the C-H stretching vibration. Consequently, the FR should be absent in the Raman spectra of the β-methanediyl group (-CDH-) and the deuterated methyl group (-CD_2H) of propanol.

E. Possible application of the molecule with single C−H/C−D bond

Although the aforementioned deuterium strategy was employed to remove the Fermi resonance in the C-H stretching vibration, it is believed that this innovative strategy can also be utilized to examine the vibrational spectra of larger molecules, including lipids, proteins, and DNA, among others. The primary obstacle to the implementation of this approach is the difficulty in synthesizing the requisite deuterated molecules. For relatively simple small molecules, the deuterated compounds can be obtained from commercial sources. However, for specific large molecules, chemists may need to develop new strategies for synthesising these new deuterated compounds.

The method discussed above was employed in the Raman spectra; however, it can also be applied in the IR spectra or sum frequency generation (SFG) spectra. In recent decades, SFG spectroscopy has demonstrated an exceptionally robust capacity to examine interfacial molecules. In the case of organic compounds, Fermi resonance frequently influences the SFG spectra within the C-H stretching region. Consequently, the introduction of new deuterated molecules with a single C−D or C−H bond can facilitate the acquisition of SFG spectra, thereby eliminating the impact of Fermi resonance.

While the Fermi resonance can be removed from spectra of molecules with a single C−H or C−D bond, this does not imply that the Fermi resonance is inherently unfavourable in all circumstances. Recent studies utilizing SFG spectroscopy have demonstrated that Fermi resonance in the C-H stretching region can be employed to investigate intermolecular interactions [20−22]. It has been observed that while the nature of the interactions undergoes a change, the frequencies of the C-H bending and stretching vibrations also fluctuate. This illustrates the sensitivity of Fermi resonance to intermolecular interactions.

The removal of the Fermi Resonance does not necessarily imply the existence of a single vibrational band in the C-H or C-D stretching region. Due to the anti-sym-

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metrical nature of the CH_3 and CH_2 groups, as well as the existence of different conformers, the vibrational bands observed in the single C-H or C-D stretching region can be assigned to specific chemical bonds. Consequently, the spectra of a molecule with a single C–H or C–D bond can be employed to quantitatively record the local structure of the molecule and the interactions.

IV. CONCLUSION

In this study, the Raman spectra of selected deuterated compounds in the C-H bending vibration and C-H stretching region were recorded through experimental means and subsequently calculated by theoretical methods. In these deuterated compounds, a single C–H bond is present in the molecule, formed by the methanetriyl group (>CH-), the deuterated methanediyl group (-CDH-), or the deuterated methyl group (-CD_2H). It was observed that the frequency of the first overtone mode of the C-H bending vibration was markedly disparate from that of the C-H stretching vibration. Consequently, Fermi resonance was absent in the C-H stretching region. Therefore, the C-H stretching Raman band can be employed to investigate the structure, interactions or dynamic properties of these particular deuterated compounds.

Supplementary materials: The theoretical Raman spectra of β-CH groups and methyl groups of *n*-propanol and various deuterated *n*-propanol in the C-H stretching vibration region were also calculated and plotted.

V. ACKNOWLEDGEMENTS

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